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Transannular Cyclization of Epoxycaryophyllenes Catalyzed by Ti^{III}: An Efficient Synthesis of Tricyclo[6.3.0.$0^{2,5}$]undecanes

Alejandro F. Barrero,*[a] M. Mar Herrador,[a] José F. Quílez del Moral,[a] Pilar Arteaga,[a] Elena M. Sánchez,[a] Jesús F. Arteaga,[a] and Maria Piedra[a]

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The transannular cyclization of epoxycaryophyllenes **2**–**7** catalyzed by Ti^{III} has been investigated. This cyclization led to alcohols **8**–**15**, all of them possessing a tricyclo[6.3.0.$0^{2,5}$]undecane skeleton. All of these compounds present pleasant aromatic properties. The cyclization takes place with high yields (> 80 %) and via the αα or ββ conformation of the intermediate radical **I**.

Introduction

β-Caryophyllene (**1**) is a sesquiterpene abundant in nature,[1–3] its main source being the oils of clove (*Eugenia caryophyllata*) and of various species of the genus *Copaifera*.[3] Its availability as a raw material and its unusual bicyclic structure have attracted the attention of organic chemists and have been the basis for the development of a wide range of cyclizations and rearrangements.[4,5] Some of these reactions have led to tricyclic derivatives of interest as fungistats[6] and as odorants in the perfume industry;[5,7–12] β-caryophyllene itself and its various hydroxylated derivatives exhibit interesting olfactive properties.[7–12] To date, publications on radical cyclizations of caryophyllenes have been scarce. Some examples are the radical-induced addition of acetaldehyde to the caryophyllene skeleton,[9] irradiation in an anionic micellar medium of β-caryophyllene (**1**) in the presence of an electron acceptor,[13] and the reduction of β-caryophyllene (**2** and **3**) and isocaryophyllene (**4** and **5**) epoxides with lithium in liquid ammonia.[14] All of these radical transformations led, with yields below 50%, to structures derived from tricyclo[6.3.0.$0^{2,5}$]undecane.

Titanocene chloride has been widely used in the radical cyclization of epoxypolyenes.[15–21] This reaction takes place under mild conditions and is tolerated by numerous functional groups (alcohols, amides, ketones, acids, esters).[21]

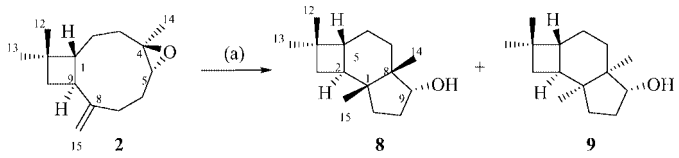
Continuing with our work on new applications of radical cyclizations of epoxyterpenoids,[19,20] we present here a study on transannular cyclizations of epoxycaryophyllenes (**2**–**7**) catalyzed by Ti^{III}. Alcohols **8**–**15** possessing a tricyclo[6.3.0.$0^{2,5}$]undecane skeleton were obtained in these processes. The overall yields of the cyclizations ranged from good to excellent.

Results and Discussion

The study of radical cyclizations of epoxycaryophyllenes began with the reaction of commercially available caryophyllene epoxide (**2**). The treatment of **2** with catalytic amounts of Cp_2TiCl in THF[20] afforded a 2:1 mixture of tricyclic alcohols **8** and **9** (95% yield) (Scheme 1).

The carbon skeleton of 1,4,4,8-tetramethyltricyclo-[6.3.0.$0^{2,5}$]undecane (4,8-cyclocaryophyllane) was established for these alcohols on the basis of their ^{1}H- and ^{13}C NMR spectra (Table 1). These NMR spectroscopic data were assigned unequivocally by two-dimensional experiments (COSY, HMQC, and HMBC). For compounds **8** and **9**, the *cis* interannular junction between the five- and six-membered rings was determined from the NOE correlations observed between the angular methyl groups on the C1- and C8 atoms. The β or α orientation of these methyl groups (Me14 and Me15) was established from their ^{13}C NMR chemical shift values (for compound **8**: δ_{Me14} = 25.4 ppm and δ_{Me15} = 17.8 ppm; for compound **9**: δ_{Me14} = 16.1 ppm and δ_{Me15} = 23.7 ppm). Additionally the β orientation of the Me14 and Me15 groups in **8** was confirmed by the NOE correlation observed between the Me15 group and the H5 proton, while the α orientation of these two methyl groups in **9** was confirmed by the NOE effect between the Me15 group and the H2 proton (Figure 1). The relative stereochemistry of the C9 atom was determined on the basis of the multiplicity observed for the H9 proton. This proton resonated as a dd, indicating a β orientation,[14] which was confirmed by the NOE effect between the H9

[a] Department of Organic Chemistry, Institute of Biotechnology, Avenida Fuentenueva, 18071 Granada, Spain
Fax: +34-958-243318
E-mail: afbarre@ugr.es



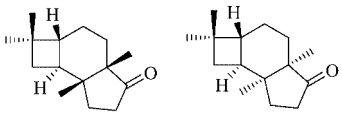
Scheme 1. Reagents and conditions: (a) Cp_2TiCl_2, Mn dust, 2,4,6-collidine, TMSCl, THF, room temp., 40 min.

proton and the Me14 group in **8** (Figure 1), whereas this NOE effect was not observed in **9**. These results indicate that the C9 atom retains the configuration of the initial epoxide. It is worth underlining that alcohols **8** and **9** had a mild aroma. Their acetylation with Ac_2O and pyridine provided acetates **8a** and **9a**, while their oxidation with PDC in DMF afforded ketones **16** and **17**, respectively. All of these compounds also presented ambergris-like aromatic properties, similar to those of 9-acetyl-1,4,4,8-tetramethyltricyclo[6.3.0.$0^{2,5}$]undecanes, products that have been described as perfume bases for different cosmetic preparations.[10,12]

Table 1. ^1H NMR and ^{13}C NMR spectroscopic data for compounds **8**–**12**, **13a** and **15**[a].

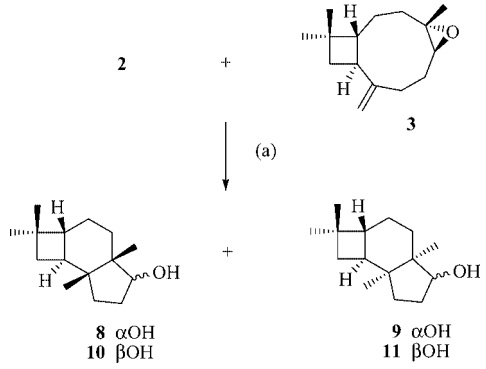
	8		**9**		**10**		**11**		**12**		**13a**		**15**	
Atom	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1		48.3		49.5		47.4		46.7		43.4		52.9[a]		45.1
2	2.11 m	39.4	1.71 m	42.4	1.61 m	41.4	1.67 dt (7.2, 11.5)	42.1	1.92 m	39.6	1.62 m	43.1	1.58 m	43.4
3	α: 1.45 m	35.8	α: 1.60 dd (7.0, 9.1)	37.5	α: 1.42 m	36.2	α: 1.50 dd (7.0, 9.2)	37.2	α: 1.40 m	35.0	α: 1.47 m	37.7	α: 1.58 m	37.3
	β: 1.34 m		β: 1.31 m		β: 1.32 m		β: 1.24 m		β: 1.40 m		β: 1.23 m		β: 1.27 m	
4		36.2		37.5		36.5		38.1		36.3				38.1
5	1.52 m	44.4	1.53 m	46.1	1.32 m	46.6	1.41 m	47.1	1.40 m	43.2	1.47 m	46.4	1.58 m	46.8
6	a: 1.52 m	24.4	a: 1.38 m	23.6	a: 1.32 m	23.2	a: 1.41 m	23.5	a: 1.40 m	21.6	a: 1.23 m	23.7	a: 1.51 m	23.5
	b: 1.34 m		b: 1.38 m		b: 1.32 m		b: 1.24 m		b: 1.40 m		b: 1.23 m		b: 1.27 m	
7	a: 1.70 m	31.8	a: 1.25 m	37.2	a: 1.61 m	31.9	a: 1.24 m	29.9	a: 1.66 m	23.4	a: 1.97 m	29.9	a: 1.99 m	23.7
	b: 1.25 m		b: 1.16 m		b: 1.12 m		b: 1.24 m		b: 1.40 m		b: 1.92 m		b: 1.95 m	
8		44.1		45.2		43.9		44.4		46.5		45.8[a]		49.3
9	β: 3.80 dd (4.6, 7.6)	85.0	β: 3.66 dd (2.7, 7.1)	82.7	α: 4.48 t (8.5)	75.7	α: 3.97 t (8.8)	81.0	β: 4.13 t (7.5)	80.9	β: 4.65 dd (1.7, 6.7)	82.5	α: 4.37 t (8.8)	80.0
10	α: 1.61 m	32.1	α: 1.71 m	32.4	α: 2.16 dq (1.6, 10.2)	30.1	α: 2.15 m	30.3	α: 1.92 m	31.4	α: 1.62 m	30.5	α: 2.17 m	28.6
	β: 2.11 m		β: 2.31 ddt (3.3, 7.0, 14.0)		β: 1.42 m		β: 1.58 m		β: 1.66 m		β: 2.25 dddd (4.0, 7.0, 11.2, 14.9)		β: 1.69 m	
11	α: 1.52 m	34.6	α: 1.38 m	30.5	α: 1.42 m	32.8	α: 1.07 m	27.5	α: 1.40 m	35.9	α: 1.23 m	31.5	α: 1.03 m	28.2
	β: 1.34 m		β: 2.01 dt (8.5, 12.9)		β: 1.32 m		β: 2.02 dt (5.1, 13.1)		β: 1.40 m		β: 2.05 dd (7.0, 13.0)		β: 2.17 m	
12	1.00 s	30.4	1.06 s	30.4	0.99 s	30.3	1.02 s	30.4	1.00 s	30.5	0.97 s	30.4	1.06 s	30.4
13	1.01 s	21.3	1.11 s	20.9	1.00 s	21.0	1.06 s	20.9	1.01 s	21.3	0.99 s	20.9	1.07 s	20.9
14	0.71 s	25.4	1.02 s	16.1	0.67 s	17.4	0.94 s	19.3	a: 3.40 d (9.5)	69.5	a: 3.69 d (9.4)	60.9	a: 3.83 d (9.2)	67.2
									b: 3.38 d (9.5)		b: 3.59 d (9.4)		b: 3.72 d (9.2)	
15	0.86 s	17.8	0.96 s	23.7	0.87 s	17.2	0.74 s	23.6	0.82 s	17.7	0.88 s	22.7	0.80 s	23.5
CO*CH*$_3$											1.93 s	21.6		
TBS									0.87 s	25.9	0.79 s	25.9	0.90 s	26.0
TBS										18.3		18.3		18.3
TBS									0.04 s	1.1	0.05 s	– 5.5	–0.02 s	– 5.5
TBS									0.01 s	– 5.5	0.03 s	– 5.6	–0.06 s	– 5.5

[a] δ in ppm, J in Hz in parentheses. Signal assignments having the same superscripted letter may be interchanged.



16 17

Encouraged by the results obtained, we continued this study with the transannular cyclization of other epoxycaryophyllene derivatives (**3**–**7**) catalyzed by Ti^{III}. The epoxidation of β-caryophyllene with *m*-CPBA in CH_2Cl_2 led to a 4:1 mixture of epoxides **2** and **3**. Treatment of this mixture with catalytic amounts of Cp_2TiCl[20] afforded tricyclic alcohols **8**–**11** in a 20:9:5:1 ratio (90% yield) (Scheme 2). Alcohols **10** and **11** were derived from minor stereoisomer **3**.



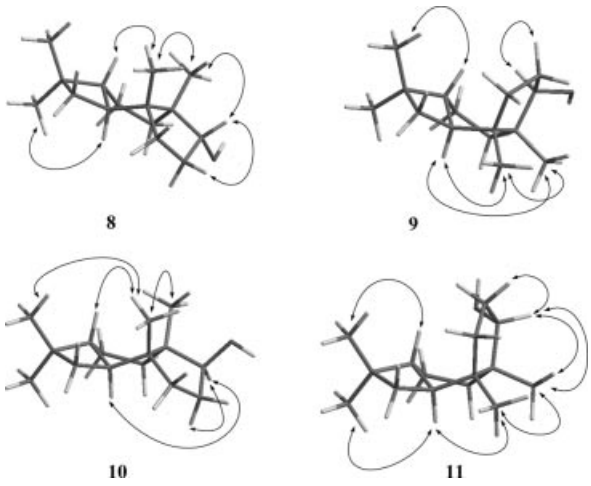
8 αOH **9** αOH
10 βOH **11** βOH

Scheme 2. Reagents and conditions: (a) Cp_2TiCl_2, Mn dust, 2,4,6-collidine, TMSCl, THF, room temp., 40 min.

The analysis of the spectroscopic data of **10** and **11** (Table 1) allowed us to establish that they are epimers of **8** and **9**, respectively, at the C9 atom. In **10** and **11**, the H9 proton appears as a triplet, which indicates an α orientation for the H9 proton at this carbon in both compounds. For compound **11**, this orientation was confirmed by the NOE effect observed between the H9 proton and the Me14 group in **11** (Figure 1). Compounds **10** and **11** were confirmed to be epimers of **8** and **9** after noticing that ketones **16** and **17** were obtained through oxidation of **8** and **9**, respectively. The acetylation of these compounds generated acetate derivatives **10a** and **11a**, which presented aromas similar to those of their epimers.

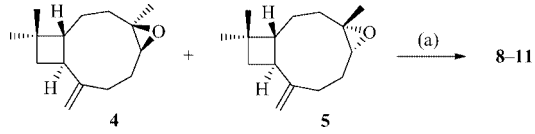
With the aim of studying the influence of changes at the epoxide stereochemistry on the outcome of these transannular cyclizations, isocaryophyllene was epoxidized with *m*-CPBA to lead to a 1:1 mixture of epoxides **4** and **5**. Treatment of this mixture with catalytic amounts of Cp_2TiCl in THF[20] again afforded tricyclic alcohols **8**–**11** (81% yield), now in a 5:2:5:1 ratio (Scheme 3). These results are similar to those obtained from **2** and **3** and permit the use of either β-caryophyllene or isocaryophyllene as starting materials for the generation of odoriferous ketones **16** and **17**.

At this point, the study focused on how the presence of oxygenated functions located α to the oxirane ring affected the selectivity of these radical cyclizations. Thus, the epoxidation of alcohol **18**, previously obtained by allyl oxidation



8 **9**
10 **11**

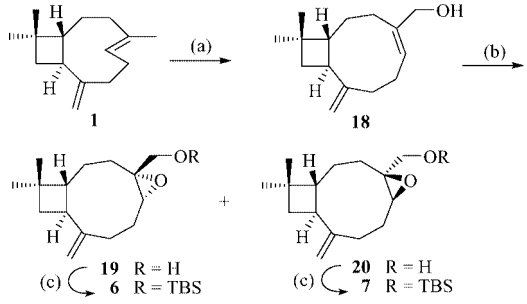
Figure 1. Selected NOEs observed for alcohols **8**–**11**.



4 **5** **8**–**11**

Scheme 3. Reagents and conditions: (a) Cp_2TiCl_2, Mn dust, 2,4,6-collidine, TMSCl, THF, room temp., 40 min.

of **1** with SeO_2,[22] afforded epoxyalcohols **19** and **20** (Scheme 4), of which **19** could be separated by column chromatography and crystallization from hexane.



1 **18**
19 R = H **20** R = H
6 R = TBS **7** R = TBS

Scheme 4. Reagents and conditions: (a) SeO_2, EtOH, room temp., 3 h. (b) *m*-CPBA, CH_2Cl_2, room temp., 220 min. (c) TBSCl, DMF, imidazole, room temp., 20 min.

The relative stereochemistry of the oxirane ring in epoxyalcohols **19** and **20** was determined from the NOE effects observed between the H14b and the H5 protons for **19** and **20**, between the H14b and the H1 protons for **19**, and between the H14b and the H9 protons for **20**. These NOE effects showed an αβ conformation for **19** and an αα conformation for **20** (Figure 2), in accordance with the nomenclature adopted for these types of sesquiterpenes.[23]

Treatment of **19** with TBSCl and imidazole in anhydrous DMF led to epoxide derivative **6**, whereas the mixture of **19** and **20** yielded **6** and **7** (Scheme 4).

The cyclization of **6** under the above conditions with Ti^{III} afforded alcohols **12** and **13** in a 10:1 proportion (93% yield) (Scheme 5). Separation of alcohol **12** was achieved by

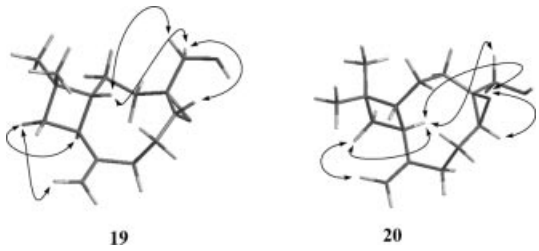
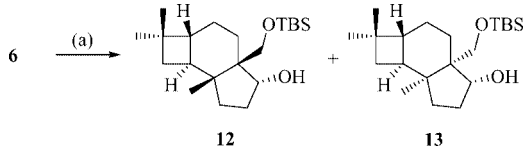


Figure 2. Selected NOEs observed for epoxyalcohols **19** and **20**.

using silica gel column chromatography, but in the case of **13**, this compound could only be isolated as its acetate derivative **13a** after semipreparative HPLC following acetylation of a mixture containing it. The NMR spectroscopic data of alcohol **12** and acetate **13a** (Table 1) were again consistent with a skeleton of 1,4,4-trimethyltricyclo[6.3.0.$0^{2,5}$]-undecan-9-ol. The stereochemistry of both **12** and **13a** was determined after comparing their spectroscopic data with those of alcohols **8**–**11** (Table 1). The exception presented by **12** in the multiplicity of the H9 signal in its ^{1}H NMR spectrum (t in place of dd) can be accounted for by the formation of an intramolecular hydrogen bond between the OH and the OTBS groups, as a result of which **12** adopts a conformation similar to that of alcohols **10** and **11** in the cyclohexane ring. The formation of the hydrogen bond was confirmed by the isolation of **12** as its 9-OTMS derivative **12b**. The H9 proton resonance in the ^{1}H NMR spectrum of derivative **12b** appeared now as a dd. Supporting the NMR spectroscopic data, theoretical calculations performed for **12** showed that the most stable conformation calculated for this compound also permits the formation of an intramolecular hydrogen bond. With regard to the different stereochemical outcomes of the reactions performed with **5** and **6**, the higher stereoselectivity observed with the latter could be rationalized by considering the steric hindrance between the CH_2OTBS and the $OTi(Cl)Cp_2$ moieties in the transition state leading to **13**.

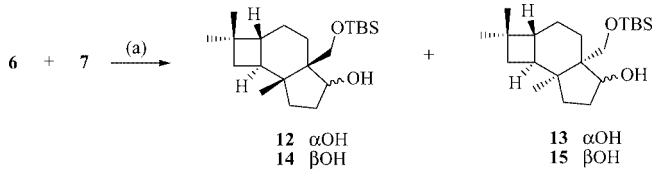


Scheme 5. Reagents and conditions: (a) Cp_2TiCl_2, Mn dust, 2,4,6-collidine, TMSCl, THF, room temp., 40 min.

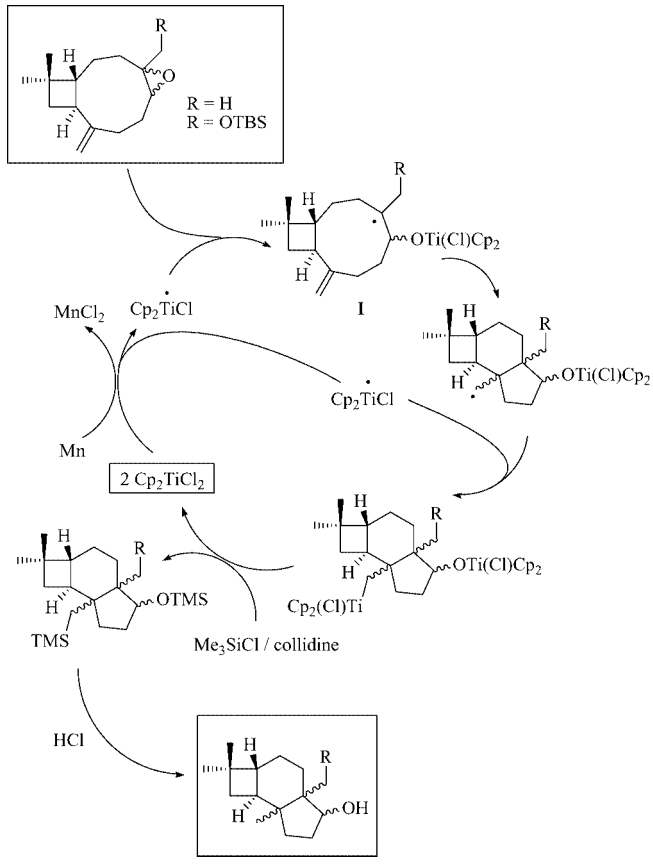
Cyclization of a 1:1 mixture of epoxy derivatives **6** and **7** under the above conditions afforded alcohols **12**–**15** in an 11:1:3:5 proportion (92% yield) (Scheme 6). The NMR spectroscopic data of **15** (Table 1) confirmed it to be an epimer of **13** at the C9 atom.

In accordance with the mechanism admitted for cyclizations catalyzed by Cp_2TiCl in the presence of the TMSCl/collidine system,[20] the catalytic cycle shown in Scheme 7 is proposed to rationalize the formation of alcohols **8**–**15**.

Following this mechanistic proposal, the stereoselectivity in the [6+5] ring closure leading to alcohols **8**–**15** should be

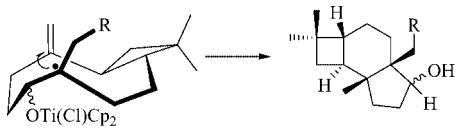


Scheme 6. Reagents and conditions: (a) Cp_2TiCl_2, Mn dust, 2,4,6-collidine, TMSCl, THF, room temp., 40 min.



Scheme 7. Catalytic cycle for the Ti^{III}-mediated radical cyclization.

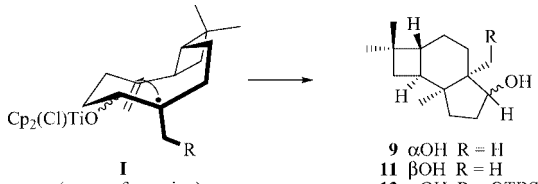
determined by how prone to cyclization the different conformations of the nine-membered ring of radical **I** are. This radical, by analogy with β-caryophyllene, presents three low-energy conformations (αα, αβ, and ββ) at room temperature.[24] The ββ conformation (exocyclic methylene and Me14 groups in the β position) provides alcohols **8**, **10**, **12**, and **14** (Scheme 8), while the αα conformation (exocyclic methylene and Me14 groups in the α position) affords alcohols **9**, **11**, **13**, and **15** (Scheme 9). A preliminary analysis by Dreiding models suggests an easier approach of the radical to the exocyclic double bond via the ββ conformer than via the αα one. Theoretical calculations of the relative energies of the products formed (Table 2) indicate a greater stability of stereoisomers **8**, **10**, **12**, and **14** versus **9**, **11**, **13**, and **15**, which confirms the stereochemical course of the reaction.



I
(ββ conformation)

8 αOH R = H
10 βOH R = H
12 αOH R = OTBS
14 βOH R = OTBS

Scheme 8. Cyclization of the ββ conformation of radical **I** to give alcohols **8**, **10**, **12**, and **14**.



I
(αα conformation)

9 αOH R = H
11 βOH R = H
13 αOH R = OTBS
15 βOH R = OTBS

Scheme 9. Cyclization of the αα conformation of radical **I** to give alcohols **9**, **11**, **13**, and **15**.

Table 2. Relative energies for compounds **8**–**15** obtained by Molecular Mechanics calculations.

Compound	E_{rel} [kcal/mol]	Compound	E_{rel} [kcal/mol]
8	0	**12**	0
9	0.4	**13**	0.8
10	0.4	**14**	0.7
11	0.7	**15**	1.6

Conclusions

In conclusion, we present an expedient and highly efficient access to tricyclic sesquiterpenoids starting from epoxycaryophyllenes by way of transannular cyclizations catalyzed by Ti^{III}. The stereoselectivities and yields obtained in these radical cyclizations are better than those found in related cationic processes.[26] The mild experimental conditions used in this reaction makes this protocol compatible with different functional groups. Additionally, some of the sesquiterpenoids obtained in these radical processes have an interesting ambergris-like aroma.

Experimental Section

General Methods: Optical rotations were measured with a 141 Perkin–Elmer polarimeter. IR spectra were recorded with a Mattson Satellite FTIR spectrometer. High-resolution MS were determined with an Autospec-Q VG-Analytical (FISONS) mass spectrometer. NMR spectra were recorded with a Bruker ARX 400 spectrometer (δ values are referenced to internal TMS). Column chromatography was carried out by using silica gel SDS 60 (35–70 μm) eluting with mixtures of hexane–MeO*t*Bu (H/E) of increasing polarity. Analytical TLC was performed on layers of silica gel Merck 60G 0.25 mm thick, using a 7% phosphomolybdic acid solution (EtOH) to visualize the spots. HPLC with UV detection was used. Semipreparative HPLC separations were carried out on a column of Spherisorb (5 μm Silica, 10 × 250 mm) with an Agilent Series 1100 instrument. Flow rate of 2.0 mL/min. The acetyl derivatives were obtained by acetylation with Ac_2O in pyridine.

Computational Details: Calculations of structures **8**–**15** were carried out with Spartan software (SGI version 5.1.1). A conformational analysis was carried out with the Spartan program by using the default Monte Carlo method, yielding 225 and 576 conformations for compounds **8**–**11** and for compounds **12**–**15**, respectively.

Oxidation of β-Caryophyllene (1) with SeO_2: A solution of SeO_2 (1.1 g, 9.9 mmol) in EtOH (10 mL) was added to a solution of **1** (2.0 g, 9.8 mmol) in EtOH (150 mL), and the mixture was stirred at room temperature for 3 h. H_2O (70 mL) was added and the mixture was extracted with MeO*t*Bu. The resulting organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried with anhydrous Na_2SO_4, filtered, and evaporated to give a crude residue, which yielded 1.1 g (55%) of isocaryophyllene and 0.9 g (42%) of **18** after chromatography (H/E, 75:25). The spectroscopic data were identical with the literature values.[22]

General Procedure for the Epoxidation Reaction to Generate 2–5, 19 and 20

3-Chloroperoxybenzoic acid (548 mg, 3.17 mmol) in anhydrous CH_2Cl_2 (14 mL) was added to a solution of **1** (508 mg, 2.45 mmol) in anhydrous CH_2Cl_2 (9 mL) under an argon atmosphere at room temperature, and the mixture was stirred for 220 min. Then, CH_2Cl_2 (50 mL) was added and was successively washed with saturated aqueous $NaHCO_3$ solution and brine, dried with anhydrous Na_2SO_4, filtered, and evaporated to give a crude residue which yielded 370 mg of a 4:1 mixture of **2** and **3** (55%) after chromatography (H/E, 95:5). The spectroscopic data were identical with the literature values.[22]

Epoxidation of Isocaryophyllene: According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 95:5) on silica gel to afford 538 mg of a 1:1 mixture of **4** and **5** (80%). The spectroscopic data were identical with the literature values.[25]

Epoxidation of 18: According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 60:40) on silica gel to afford a 1:1 mixture of **19** and **20** (60%).The crystallization of this mixture in hexane yielded **19** (186 mg), **20** (10 mg), and **19**+**20** (1020 mg).

4α,5α-Epoxy-4,5-dihydrocaryophyllen-14-ol (19): $[\alpha]_D^{20}$ = +30.1 (c = 1, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3291, 3066, 2964, 2941, 2921, 2859, 1631, 1461, 1367, 1073, 1033, 1018, 883, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.85 (br. s, 1 H, 15a-H), 4.82 (br. s, 1 H, 15b-H), 3.77 (d, J = 12.2 Hz, 1 H, 14a-H), 3.49 (d, J = 12.2 Hz, 1 H, 14b-H), 2.97 (dd, J = 3.2, 10.9 Hz, 1 H, 5-H), 2.47 (q, J = 9.0 Hz, 1 H, 9-H), 2.25 (m, 3 H, 3a-H, 3b-H, 6a-H), 1.96 (dt, J = 3.6, 9.6 Hz, 1 H, 7a-H), 1.86 (m, 2 H, 1-H, 10a-H), 1.58–1.35 (m, 5 H, 2a-H, 2b-H, 6b-H, 7b-H, 10b-H), 1.03 (s, 3 H, 13-H), 0.97 (s, 3 H, 12-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1 (C-8), 111.0 (C-15), 63.8 (C-14), 63.1 (C-4), 60.6 (C-5), 48.7 (C-1), 40.8 (C-10), 37.9 (C-9), 33.4 (C-11), 30.2 (C-3), 29.9 (C-13), 26.8 (C-6), 23.8 (C-7), 23.5 (C-2), 22.7 (C-12) ppm. FAB HRMS: calcd. for $C_{15}H_{24}O_2Na$ $[M + Na]^+$ 259.1674; found 259.1670.

4β,5β-Epoxy-4,5-dihydrocaryophyllen-14-ol (20): $[\alpha]_D^{20}$ = –3.4 (c = 1, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3438, 3070, 2948, 2926, 2861, 1632, 1456, 1366, 1072, 1029, 891, 829, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.80 (d, J = 2.1 Hz, 1 H, 15a-H), 4.70 (br. s, 1 H, 15b-H), 3.78 (d, J = 12.3 Hz, 1 H, 14a-H), 3.50 (d, J = 12.3 Hz, 1 H, 14b-H), 2.99 (dd, J = 2.8, 11.7 Hz, 1 H, 5-H), 2.60 (q, J = 9.7 Hz, 1 H, 9-H), 2.54 (m, 1 H, 3a-H), 2.31 (m, 1 H, 3b-H), 2.17 (m, 2 H, 2a-H, 6a-H), 1.81 (m, 1 H, 1-H), 1.74 (dd, J = 8.6, 10.6 Hz, 1 H, 10a-H), 1.65 (m, 1 H, 2b-H), 1.55 (m, 2 H, 7a-H, 10b-H), 1.31 (m, 2 H, 6a-H, 7b-H), 0.99 (s, 3 H, 13-H), 0.97 (s, 3 H, 12-H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 150.4 (C-8), 112.8 (C-15), 64.7 (C-14), 64.0 (C-4), 61.1 (C-5), 50.9 (C-1), 44.3 (C-9), 40.7 (C-10), 34.6 (C-11), 29.9 (C-13), 29.5 (C-3), 29.0 (C-6), 25.0 (C-7), 24.2 (C-2), 21.6 (C-12) ppm. FAB HRMS: calcd. for $C_{15}H_{24}O_2Na$ $[M+Na]^+$ 259.1674; found 259.1669.

General Procedure for the Protection of Epoxyalcohols 19 and 20

Imidazole (77.2 mg, 1.13 mmol) was added to a solution of the epoxyalcohol (0.48 mmol) in anhydrous DMF (4 mL) at room temperature, and the mixture was stirred for 20 min, TBDMSCl (148 mg, 0.98 mmol) was then added. After 15 min, MeO*t*Bu (10 mL) was added. The solution was successively washed with HCl (2 N) and brine. The organic phase was dried with anhydrous Na_2SO_4 and concentrated to give a crude residue.

14-*tert*-Butyldimethylsilyloxymethyl-4α,5α-epoxy-4,5-dihydrocaryophyllene (6): According to the general procedure from epoxyalcohol **19**, the resulting crude product was purified by column chromatography (H/E, 96:4) on silica gel to afford 237 mg (86%) of **6**. $[\alpha]_D^{20}$ = +14.4 (c = 1, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3070, 2951, 2928, 2857, 1633, 1459, 1364, 1253, 1123, 1100, 837, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.79 (br. s, 1 H, 15a-H), 4.76 (br. s, 1 H, 15b-H), 3.85 (d, J = 11.7 Hz, 1 H, 14a-H), 3.24 (d, J = 11.7 Hz, 1 H, 14b-H), 2.69 (dd, J = 2.9, 11.3 Hz, 1 H, 5-H), 2.42 (q, J = 8.8 Hz, 1 H, 9-H), 2.19 (m, 3 H, 3a-H, 3b-H, 6a-H), 2.04 (ddd, J = 2.5, 5.0, 13.4 Hz, 1 H, 7a-H), 1.83 (m, 1 H, 1-H), 1.79 (dd, J = 8.7, 10.9, 1 H, 10a-H), 1.56–1.19 (m, 5 H, 2a-H, 2b-H, 6b-H, 7b-H, 10b-H), 0.99 (s, 3 H, 13-H), 0.92 (s, 3 H, 12-H), 0.83 [s, 9 H, $SiC(CH_3)_3$], 0.00 (s, 3 H, $SiCH_3$), –0.01 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4 (C-8), 110.8 (C-15), 66.3 (C-14), 63.6 (C-4), 60.3 (C-5), 49.3 (C-1), 40.9 (C-10), 37.7 (C-9), 33.5 (C-11), 30.9 (C-3), 30.1 (C-13), 26.7 (C-6), 25.9 [$SiC(CH_3)_3$], 23.9 (C-7), 23.5 (C-2), 22.9 (C-12), 18.4 [$SiC(CH_3)_3$], –5.2 ($SiCH_3$), –5.4 ($SiCH_3$) ppm. FAB HRMS: calcd. for $C_{21}H_{38}O_2SiNa$ $[M+Na]^+$ 373.2539; found 373.2535.

14-*tert*-Butyldimethylsilyloxymethyl-4β,5β-epoxy-4,5-dihydrocaryophyllene (7): According to the general procedure from epoxyalcohol **20**, the resulting crude product was purified by column chromatography (H/E, 96:4) on silica gel to afford 12 mg (80%) of **7**. $[\alpha]_D^{20}$ = –2.0 (c = 1, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3069, 2951, 2929, 2858, 1631, 1461, 1364, 1253, 1125, 1099, 1056, 837, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.79 (d, J = 2.2 Hz, 1 H, 15a-H), 4.68 (d, J = 2.2 Hz, 1 H, 15b-H), 3.94 (d, J = 11.8 Hz, 1 H, 14a-H), 3.31 (d, J = 11.8 Hz, 1 H, 14b-H), 2.81 (dd, J = 2.7, 11.6 Hz, 1 H, 5-H), 2.64 (q, J = 9.7 Hz, 1 H, 9-H), 2.57 (m, 1 H, 3a-H), 2.34 (m, 1 H, 3b-H), 2.12 (m, 2 H, 2a-H, 6a-H), 1.82 (m, 1 H, 1-H), 1.73 (m, 1 H, 10a-H), 1.56 (m, 2 H, 7a-H, 10b-H), 1.42 (dt, J = 2.8, 11.2 Hz, 1 H, 7b-H), 1.14 (dt, J = 2.8, 13.7 Hz, 1 H, 6b-H), 1.01 (s, 3 H, 13-H), 1.00 (s, 3 H, 12-H), 0.91 [s, 9 H, $SiC(CH_3)_3$], 0.07 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2 (C-8), 112.5 (C-15), 66.4 (C-14), 64.2 (C-4), 60.5 (C-5), 50.5 (C-1), 44.3 (C-9), 40.4 (C-10), 34.5 (C-11), 29.8 (C-13), 29.3 (C-3), 28.1 (C-6), 25.8 [$SiC(CH_3)_3$], 25.1 (C-7), 23.9 (C-2), 21.5 (C-12), 18.3 [$SiC(CH_3)_3$], –5.2 ($SiCH_3$), –5.5 ($SiCH_3$) ppm. FAB HRMS: calcd. for $C_{21}H_{38}O_2SiNa$ $[M+Na]^+$ 373.2539; found 373.2535.

General Procedure for the Transannular Cyclization of Epoxycaryophyllenes (8–15)

Strictly deoxygenated THF (30 mL) was added to a mixture of Cp_2TiCl_2 (0.41 mmol) and Mn dust (16.5 mmol) under an argon atmosphere, and the suspension was stirred at room temperature until it turned lime green (after about 15 min.). Then, a solution of epoxide (2.06 mmol) and 2,4,6-collidine (15.9 mmol) in THF (3 mL), and TMSCl (9.09 mmol) were added, and the solution was stirred for 40 min. The reaction was then quenched with HCl (2 N) and extracted with MeO*t*Bu. The organic phase was washed with brine, dried (anhydrous Na_2SO_4), and the solvent was removed. Products obtained were isolated by column chromatography of the crude residue on silica gel (H/E).

(1*R*,2*S*,5*R*,8*S*,9*R*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9α-ol (8): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 97:3) on silica gel to afford **8** [297 mg (65%) from **2**, 233 mg (51%) from **2**+**3**, and 137 mg (30%) from **4**+**5**]. $[\alpha]_D^{20}$ = –4.2 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3338, 2957, 2921, 2862, 1452, 1380, 1256, 1048 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. EI HRMS: calcd. for $C_{14}H_{21}$ $[M-H_2O-CH_3]^+$ 189.1643; found 189.1642.

(1*R*,2*S*,5*R*,8*S*,9*R*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9α-yl Acetate (8a): $[\alpha]_D^{20}$ = –5.4 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2956, 2925, 2863, 1738, 1455, 1363, 1240, 1039, 1019 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.88 (dd, J = 3.3, 8.0 Hz, 1 H, 9-H), 2.20 (m, 2 H), 2.06 (s, 3 H, $COCH_3$) 1.71–1.21 (m, 10 H), 1.04 (s, 3 H, 13-H), 1.01 (s, 3 H, 12-H), 0.87 (s, 3 H, 15-H), 0.76 (s, 3 H, 14-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7 ($CO$$CH_3$), 86.1 (C-9), 48.2 (C-1), 44.8 (C-5), 44.6 (C-8), 38.6 (C-2), 36.2 (C-4), 35.9 (C-3), 34.3 (C-11), 32.4 (C-7), 30.4 (C-12), 30.2 (C-10), 25.2 (C-14), 24.4 (C-6), 21.6 (COCH_3), 21.1 (C-13), 16.9 (C-15) ppm. FAB HRMS: calcd. for $C_{17}H_{28}O_2Na$ $[M+Na]^+$ 287.1987; found 287.1984.

(1*S*,2*S*,5*R*,8*R*,9*R*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9α-ol (9): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 95:5) on silica gel to afford **9** [137 mg (30%) from **2**, 100 mg (22%) from **2**+**3**, and 55 mg (12%) from **4**+**5**]. $[\alpha]_D^{20}$ = +10.8 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3395, 2996, 2930, 2862, 1457, 1365, 1255, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. EI HRMS: calcd. for $C_{14}H_{21}$ $[M-H_2O-CH_3]^+$ 189.1643; found 189.1647.

(1*S*,2*S*,5*R*,8*R*,9*R*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9α-yl Acetate (9a): $[\alpha]_D^{20}$ = +11.3 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2950, 2927, 2861, 1737, 1457, 1366, 1246, 1021 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.69 (dd, J = 2.5, 7.4 Hz, 1 H, 9-H), 2.30 (m, 1 H), 2.02 (s, 3 H, $COCH_3$), 2.01 (m, 1 H), 1.67 (m, 2 H), 1.51 (m, 2 H), 1.26 (m, 6 H), 1.06 (s, 3 H, 13-H), 1.01 (s, 3 H, 12-H), 0.90 (s, 3 H, 14-H), 0.87 (s, 3 H, 15-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$,): δ = 170.8 ($CO$$CH_3$), 84.0 (C-9), 49.2 (C-1), 46.2 (C-5), 45.6 (C-8), 42.0 (C-2), 41.2 (C-4), 37.6 (C-3), 36.9 (C-7), 30.4 (C-11, C-12), 30.1 (C-10), 23.6 (C-6), 22.9 (C-15), 21.4 (COCH_3), 20.8 (C-13), 16.0 (C-14) ppm. FAB HRMS: calcd. for $C_{17}H_{28}O_2Na$ $[M+Na]^+$ 287.1987; found 287.1989.

(1*R*,2*S*,5*R*,8*S*,9*S*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9β-ol (10): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 95:5) on silica gel to afford **10** [55 mg (12%) from **2**+**3** and 137 mg (30%) from **4**+**5**]. $[\alpha]_D^{20}$ = +38.8 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3406, 2952, 2923, 2864, 1455, 1259, 1097, 1044 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. EI HRMS: calcd. for $C_{14}H_{21}$ $[M-H_2O-CH_3]^+$ 189.1643; found 189.1645.

(1*R*,2*S*,5*R*,8*S*,9*S*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9β-yl Acetate (10a): $[\alpha]_D^{20}$ = +39.5 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2952, 2925, 2868, 1735, 1458, 1363, 1246, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.45 (dd, J = 7.0, 9.2 Hz, 1 H, 9-H), 2.25

(m, 1 H), 2.03 (s, 3 H, $COCH_3$), 1.71 (m, 2 H), 1.53–1.07 (m, 9 H), 1.03 (s, 3 H, 13-H), 1.00 (s, 3 H, 12-H), 0.89 (s, 3 H, 15-H), 0.75 (s, 3 H, 14-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.3 ($CO CH_3$), 89.8 (C-9), 47.0 (C-1), 45.5 (C-5), 43.8 (C-8), 41.2 (C-2), 36.5 (C-4), 36.2 (C-3), 33.0 (C-11), 32.1 (C-7), 30.3 (C-12), 26.9 (C-10), 23.2 (C-6), 21.3 ($CO CH_3$), 21.0 (C-13), 18.6 (C-14), 16.8 (C-15) ppm. FAB HRMS: calcd. for $C_{17}H_{28}O_2Na$ $[M+Na]^+$ 287.1987; found 287.1990.

(1*S*,2*S*,5*R*,8*R*,9*S*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9β-ol (11): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 90:10) on silica gel to afford **11** [11 mg (2.5%) from **2**+**3** and 27 mg (6%) from **4**+**5**]. $[\alpha]_D^{20}$ = +26.2 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3242, 2952, 2921, 2865, 1455, 1365, 1262, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. EI HRMS: calcd. for $C_{14}H_{21}$ $[M-H_2O-CH_3]^+$ 189.1643; found 189.1639.

(1*S*,2*S*,5*R*,8*R*,9*S*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9β-yl Acetate (11a): $[\alpha]_D^{20}$ = +27.9 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2950, 2929, 2861, 1740, 1456, 1370, 1245, 1051, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.94 (t, J = 8.7 Hz, 1 H, 9-H), 2.25 (m, 1 H), 2.10 (m, 1 H), 2.01 (s, 3 H, $COCH_3$), 1.71–1.09 (m, 10 H), 1.07 (s, 3 H, 13-H), 1.03 (s, 3 H, 12-H), 0.93 (s, 3 H, 14-H), 0.79 (s, 3 H, 15-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4 ($CO CH_3$), 82.6 (C-9), 46.9 (C-5), 46.6 (C-1), 44.2 (C-8), 41.7 (C-2), 38.1 (C-4), 37.3 (C-3), 31.4 (C-7), 30.4 (C-12), 27.8 (C-11), 26.8 (C-10), 22.5 (C-6), 23.2 (C-15), 21.3 ($CO CH_3$), 20.8 (C-13), 19.3 (C-14) ppm. FAB HRMS: calcd. for $C_{17}H_{28}O_2Na$ $[M+Na]^+$ 287.1987; found 287.1988.

(1*R*,2*S*,5*R*,8*S*,9*R*)-8-(*tert*-Butyldimethylsilyloxy)methyl-1,4,4-trimethyltricyclo[6.3.0.0^{2,5}] undecan-9α-ol (12): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 90:10) on silica gel to afford **12** [623 mg (86%) from **6** and 355 mg (49%) from **6**+**7**]. $[\alpha]_D^{20}$ = –8.2 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3421, 2954, 2925, 2858, 1461, 1259, 1097, 1027, 838 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. FAB HRMS: calcd. for $C_{21}H_{40}O_2SiNa$ $[M+Na]^+$ 375.2695; found 375.2698.

(1*R*,2*S*,5*R*,8*S*,9*R*)-8-(*tert*-Butyldimethylsilyloxy)methyl-1,4,4-trimethyl-9α-trimethylsilyloxytricyclo[6.3.0.0^{2,5}]undecane (12b): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 100:0) on silica gel and HPLC (H/E, 100:0) to afford 25 mg (3%) of **12b**. $[\alpha]_D^{20}$ = –11.8 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2929, 2859, 1462, 1251, 1073, 1017, 905, 838 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.21 (dd, J = 3.3, 7.8 Hz, 1 H, 9-H), 3.21 (d, J = 9.6 Hz, 1 H, 14a-H), 3.12 (d, J = 9.6 Hz, 1 H, 14b-H), 2.19 (dt, J = 7.4, 11.6 Hz, 1 H, 2-H), 2.05 (m, 1 H, 10β-H), 1.78 (ddd, J = 1.9, 4.7, 14.1 Hz, 1 H, 7α-H), 1.61 (m, 2 H, 6a-H, 10α-H), 1.46–1.26 (m, 5 H, 3a-H, 3b-H, 5-H, 11a-H, 11b-H), 0.99 (s, 6 H, 12-H, 13-H), 0.92 (m, 2 H, 6b-H, 7β-H), 0.86 [s, 12 H, 15-H, $SiC(CH_3)_3$], 0.04 (s, 3 H, $SiCH_3$), 0.02 (s, 3 H, $SiCH_3$), 0.00 [s, 9 H, $Si(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.7 (C-9), 69.3 (C-14), 45.0 (C-5), 44.1 (C-8), 39.0 (C-2), 36.1 (C-1), 35.3 (C-3)[a], 35.1 (C-11)[a], 34.0 (C-10), 30.4 (C-12), 29.8 (C-4), 28.5 (C-7), 26.2 [$SiC(CH_3)_3$], 24.4 (C-6), 21.1 (C-15), 18.3 [$SiC(CH_3)_3$], 15.9 (C-13), 0.0 [$Si(CH_3)_3$], –2.6 ($SiCH_3$), –5.5 ($SiCH_3$) ppm (values with the same superscripted letter are interchangeable). FAB HRMS: calcd. for $C_{24}H_{49}O_2Si_2$ $[M+H]^+$ 425.3271; found 425.3271.

(1*S*,2*S*,5*R*,8*R*,9*R*)-8-(*tert*-Butyldimethylsilyloxy)methyl-1,4,4-trimethyltricyclo[6.3.0.0^{2,5}] undecan-9α-yl Acetate (13a): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 90:10) on silica gel and acetylated. The acetylated crude product was purified by column chromatography (H/E, 97:3) on silica gel and HPLC (H/E, 98.5:1.5) to afford **13a** [40 mg (5%) from **6** and 24 mg (3%) from **6**+**7**]. $[\alpha]_D^{20}$ = +14.3 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2954, 2929, 2860, 1739, 1461, 1374, 1256, 1098, 1019, 859, 834, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. FAB HRMS: calcd. for $C_{23}H_{42}O_3SiNa$ $[M+Na]^+$ 417.2801; found 417.2803.

(1*S*,2*S*,5*R*,8*R*,9*S*)-8-(*tert*-Butyldimethylsilyloxy)methyl-1,4,4-trimethyltricyclo[6.3.0.0^{2,5}]undecan-9β-ol (15): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 90:10) on silica gel to afford 159 mg (22%) of **15**. $[\alpha]_D^{20}$ = +29.2 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3440, 2952, 2929, 2859, 1470, 1257, 1081, 837, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$): δ = see Table 1. FAB HRMS: calcd. for $C_{21}H_{40}O_2SiNa$ $[M+Na]^+$ 375.2695; found 375.2698.

General Procedure for the Oxidation of 8–11

Preparation of 16 and 17: PDC (1.41 g, 3.75 mmol) was added to a solution of the alcohol (0.12 g, 0.54 mmol) in anhydrous DMF (5 mL) at 0 °C. After 8 h, *tert*-butyl methyl ether (50 mL) was added. The solution was washed with brine. The organic phase was dried (anhydrous Na_2SO_4) and concentrated to give a crude residue. Products obtained were isolated by column chromatography of the crude residue on silica gel (H/E).

(1*R*,2*S*,5*R*,8*S*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9-one (16): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 95:5) on silica gel to afford 59 mg (50%) of **16**. $[\alpha]_D^{20}$ = +121.1 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2951, 2928, 2865, 1738, 1456, 1365, 1267, 1098 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (m, 2 H, 6a-H, 7a-H), 1.97 (dt, J = 3.0, 13.6 Hz, 1 H, 6b-H), 1.59 (m, 2 H), 1.46 (dd, J = 7.2, 9.5 Hz, 1 H, 3a-H), 1.38 (m, 2 H), 1.27 (m, 2 H), 1.12 (m, 2 H), 0.97 (s, 6 H, 12-H, 13-H), 0.92 (s, 3 H, 15-H), 0.75 (s, 3 H, 14-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 222.9 (C-9), 54.1(C-8), 45.3 (C-5), 43.0 (C-1), 41.3 (C-2), 36.6 (C-4), 35.9 (C-3), 33.2 (C-10), 30.4 (C-7), 30.2 (C-12), 28.4 (C-11), 24.5 (C-6), 20.8 (C-13), 20.5 (C-14), 16.0 (C-15) ppm. EI HRMS: calcd. for $C_{15}H_{24}O$ $[M]^+$ 220.1827; found 220.1826.

(1*S*,2*S*,5*R*,8*R*)-1,4,4,8-Tetramethyltricyclo[6.3.0.0^{2,5}]undecan-9-one (17): According to the general procedure, the resulting crude product was purified by column chromatography (H/E, 95:5) on silica gel to afford 59 mg (50%) of **17**. $[\alpha]_D^{20}$ = +2.5 (c = 1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2961, 2891, 1740, 1442, 1367, 1189, 1065 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (m, 1 H), 2.24 (m, 2 H), 1.74 (m, 1 H), 1.59 (m, 2 H), 1.31 (m, 6 H), 1.06 (s, 3 H, 13-H), 1.03 (s, 3 H, 12-H), 0.93 (s, 3 H, 14-H), 0.76 (s, 3 H, 15-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 222.7 (C-9), 53.5 (C-8), 46.3 (C-5), 43.7 (C-1), 41.4 (C-2), 38.3 (C-4), 36.7 (C-3), 34.6 (C-8), 33.0 (C-7), 30.4 (C-12), 25.7 (C-11), 23.2 (C-6), 22.4 (C-15), 20.6 (C-13), 15.6 (C-14) ppm. EI HRMS: calcd. for $C_{15}H_{24}O$ $[M]^+$ 220.1827; found 220.1825.

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